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Abstract
Photoinduced phenomena are of general interest for new materials. Recently,
photoinduced molecular desorption of oxygen has been reported in carbon
nanotubes. Here we present, using thermopower measurements, that carbon
nanotubes when exposed simultaneously to UV light and oxygen exhibit
photoinduced oxidation of the nanotubes. At least two plausible mechanisms
for the experimentally observed photoinduced oxidation are proposed: (i) a
lower energy barrier for the adsorption of photo-generated singlet oxygen, or
(ii) due to the presence of defects in carbon nanotubes that may facilitate
the formation of locally electron-deficient and electron-rich regions on the
nanotubes which facilitate the adsorption of oxygen molecules on the nanotubes.

(Some figures in this article are in colour only in the electronic version)

The sign of the thermopower (TEP) has been found to be extremely sensitive to oxygen
adsorption in single-walled carbon nanotube (SWNT) bundles [1–3]. Room temperature TEP
values around $+45\ \mu\mathrm{V\ K^{-1}}$ have been reported in 'mats' of SWNT bundles doped with oxygen
to a saturation doping concentration under ambient conditions. Upon desorbing oxygen from
the SWNT bundles at elevated temperatures (350–500 K) and high vacuum (10^{-5}–10^{-8} Torr)
over a period of $\sim$0.5–12 h, the TEP switches reversibly to an n-type value of $\sim -50\ \mu\mathrm{V\ K^{-1}}$
[1–3]. Under ambient conditions, the time evolution (t_{sat}) from negative TEP values in oxygen-
desorbed SWNT mats to positive TEP values has been measured to be of the order of a few
minutes to hours, depending on the mat thickness [1–3]. Recently, p-type carbon nanotube

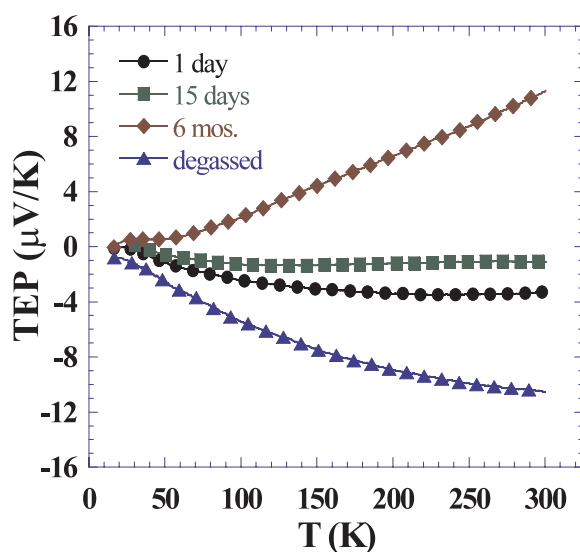[7] Author to whom any correspondence should be addressed.

Figure 1. Evolution of temperature-dependent TEP for a MWNT film exposed to air in room light.

field effect transistors (p-CNTFETs) when annealed in vacuum were found to convert to n-CNTFETs [4]. Upon re-exposure to oxygen, the p-CNTFETs properties were recovered [4]. In this paper, we present experimental evidence for photoinduced oxidation of multiwalled carbon nanotubes which suggest that nanotubes may possess interesting photochemical properties.

Multiwalled carbon nanotube (MWNT) films with thickness $\sim$80 μm were prepared on quartz substrates (0.5 cm $\times$ 0.25 cm) from a thermal decomposition of a xylene–ferrocene mixture [5]. The dominant outer tube diameter in the sample ranged between $\sim$20 and 30 nm. One of the freshly prepared air-exposed films was mounted immediately after preparation onto our standard sample-mounting device for measuring its TEP properties in the temperature range from 10 to 300 K. The device consisted primarily of two copper blocks between which the film was supported using silver epoxy. A small heater mounted on one of the blocks provided the temperature gradient across the film for TEP measurements. The device was placed inside a closed cycle refrigerator, evacuated to $\sim$10^{-6} Torr, and the MWNT film's TEP data were collected during the cooling and warming cycles from 10 to 300 K. A room temperature TEP value of $\sim$−10 μV K^{-1} is observed in freshly prepared or degassed nanotube films, indicating that the MWNTs are n type (figure 1). Subsequently, the MWNT film was exposed to room light and room air and its TEP values were measured until the film attained a saturated doping concentration of oxygen. After one day of exposure to ambient conditions, the MWNT film exhibited a room temperature TEP value of $\sim$−4 μV K^{-1} (figure 1). As the film aged over a period of 4–6 months in room air and room light, the TEP gradually changed to positive values and reached +12 μV K^{-1} in the oxygen saturated film (figure 1). Similar changes in the sign of the free carriers as a function of oxygen adsorption in SWNT bundles have previously been reported [2, 3]. It should be noted that the magnitude of the room temperature TEP in SWNT bundles is higher ($\sim$40 μV K^{-1}) while that of graphite is lower ($\sim$4 μV K^{-1}) compared to that of MWNT films ($\sim$12 μV K^{-1}). This observation is a result of the fact that TEP is directly proportional to the carrier density. It is also important to note that the timescale over which the MWNT films attain oxygen saturation is much larger ($t_{sat} \sim$ 6 months) than the
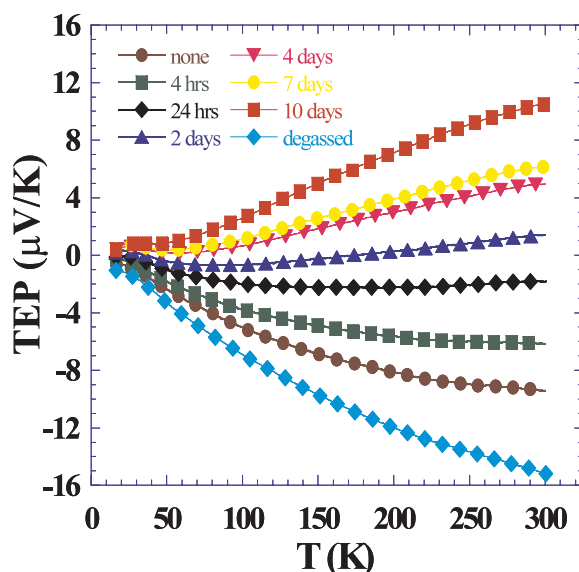
Figure 2. Temperature-dependent TEP data for a MWNT film exposed simultaneously to air and UV light. The trace indicated as 'none' corresponds to the response of an as-prepared MWNT film. This film was subsequently degassed and then systematically exposed to air and UV light.

corresponding timescale for SWNT bundles ($t_{sat} \sim$ few hours to days). Thus, MWNTs offer a unique opportunity to study photoinduced adsorption of oxygen in a quasi-1D carbon system. Next, the oxygen was desorbed reversibly from this MWNT film (at 400 K and 10^{-5} Torr vacuum for 12 h) and the negative TEP values were recovered in the degassed film, suggesting that oxygen can be reversibly desorbed from the MWNT films (figure 1).

In another degassed MWNT film, the TEP values were monitored as a function of exposure to UV radiation in room air ($\lambda = 240$ nm; power density of ~ 4 μW mm^{-2}). Very low UV power was used in our experiments to avoid sample heating due to incident illumination. The motivation for this part of the work was to determine whether the presence of UV light leads to photoinduced diffusion of oxygen into the MWNT films. Similar to the air/room light exposed films, the sign of the TEP becomes positive in the presence of air/UV radiation. Importantly, the rate at which the TEP sign reverses (and saturates) is greatly accelerated (figure 2). In figure 3, the room temperature TEP values for air/room light-exposed and air/UV-exposed MWNT films are plotted as the films attain the saturated TEP value. The broken curves serve as guides to the eye. Gauging from the times taken to swing from ~ -12 to ~ 0 μV K^{-1} (indicated by the downward pointing arrows in figure 3), we estimate that the UV illumination enhances the oxidation rate by at least a factor of ~ 30. Similar results were obtained when these experiments were performed in an oxygen atmosphere instead of air.

We propose two mechanisms by which UV illumination could enhance the oxidation of carbon nanotubes. To model the oxygen–nanotube interaction, we consider an oxygen molecule in the presence of a semiconducting (10, 0) SWNT. We use a periodically repeated supercell containing a section of the nanotube with 120 atoms. When an oxygen molecule is added to this cell the distance between periodic replicas of the molecule is large enough to avoid spurious interactions. We use density-functional theory (DFT) [6] within a plane wave pseudopotential framework and adopt a molecular dynamics approach to deal efficiently with nuclear relaxation and dynamics [7]. DFT correctly predicts that the ground state of an
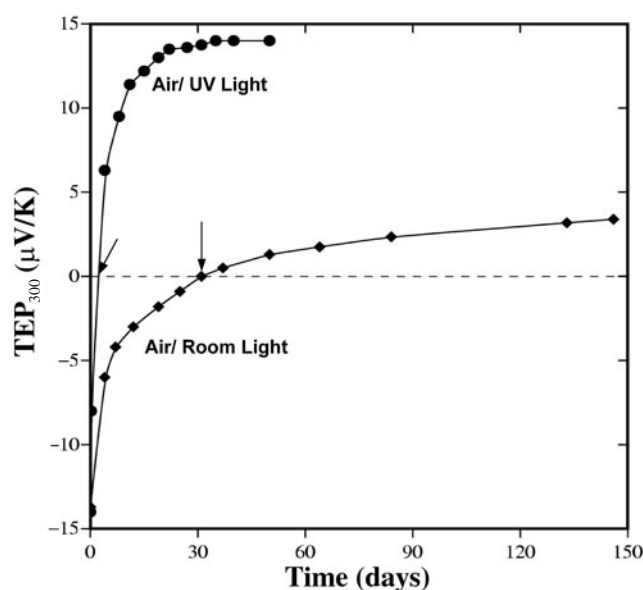
Figure 3. Room temperature TEP values plotted as a function of time for a MWNT film exposed to air in the presence (circles) or absence (diamonds) of UV light.

isolated O_2 molecule is a spin triplet (T). We find that, when an oxygen molecule approaches a nanotube, it retains its spin polarized state [8]. As a consequence of the spin splitting the oxygen molecule remains in a closed shell configuration and exhibits only a weak interaction with the nanotube[8]. The weak binding energy for triplet oxygen does not depend significantly on the curvature of the nanotube and essentially similar results are found for an O_2 molecule interacting with a planar graphene sheet [9]. The charge transfer between a molecule and a nanotube can be quantified by Mulliken population analysis. We find that, in the case of a physisorbed spin-polarized (triplet) oxygen molecule located at the equilibrium distance from a (10, 0) nanotube, the charge transfer is negligible (∼0.01e) and cannot account for the experimentally observed effects attributed to oxygen absorption on the TEP. A stronger interaction, associated with chemisorption, must be invoked to account for the experimental findings discussed in figures 1–3.

A possible existence of a chemisorbed activated singlet (S) state for oxygen on nanotubes was recently suggested on the basis of density-functional calculations [10] and is confirmed by our calculations. The nanotube's surface favours the formation of the chemisorbed S oxygen state but, on *structurally perfect* nanotubes, the chemisorbed S state has considerably higher energy than the physisorbed T state, even for small nanotube radii. For instance, in the case of a (10, 0) SWNT, we find that the S state is higher than the T state by approximately 0.8 eV, resulting in a negligible thermal occupation at room temperature. However, this picture changes drastically if native nanotube defects are taken into account. The most likely defects in nanotubes correspond to topological modifications of the hexagonal carbon network. Two simple examples are the Stone–Wales defect and the 7–5–5–7 defects in which carbon hexagons

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[8] We find that the binding energy of the molecule and its equilibrium separation from the nanotube can vary significantly, depending on the use of the local density approximation (LDA) or a generalized gradient approximation (GGA) for the exchange and correlation energy. This is not surprising since the binding is due to van der Waals interactions that are not well described by current DFT functionals.
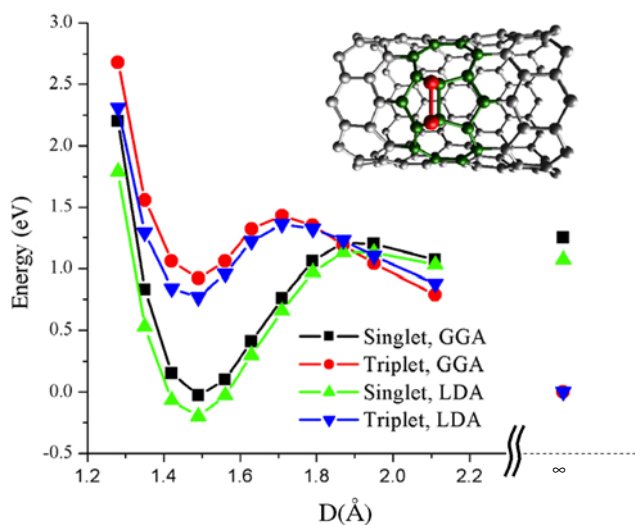
Figure 4. Plots of binding energy of O_2 with a (10, 0) nanotube as a function of the molecule's distance D (Å) from the nanotube surface. The binding energy of the physisorbed T state is about 0.004 eV at 3.7 Å (not shown here [9]). The inset shows a ball and stick picture of O_2 (large atoms) bonded to a 7–5–5–7 (small atoms) defect site. See the text for details.

are replaced by heptagons and pentagons [11]. The strained carbon bonds of the defect favour S oxygen chemisorption. In the case of a (10, 0) SWNT, for instance, we find that the chemisorbed S state is higher than the physisorbed T state by 0.3 eV only in the presence of a Stone–Wales defect, while the S state becomes energetically slightly favoured (by 0.03 eV within GGA [12]) compared to the physisorbed T state in the presence of a 7–5–5–7 defect. The potential energy profile corresponding to the chemisorbed T and S states of an oxygen molecule approaching a 7–5–5–7 defect site on a (10, 0) SWNT is shown in figure 4. The energy barrier for oxygen in the T state as estimated from figure 4 is ∼1.4 eV. For oxygen in the S state, a relatively negligible energy barrier is observed (see figure 4) which consequently is responsible for the enhanced oxidation of nanotubes.

Notice that both LDA [13] and GGA predict a substantially similar behaviour. While the energies of the local minima result from unconstrained minimization, the transition state energies are upper bounds obtained by constraining the system along an approximate reaction coordinate. Based on extensive constrained calculations and on free dynamical simulations at the local minima and at approximate saddle points, we do not expect an error substantially larger than 0.1 eV in our estimated energy barriers due to our imperfect knowledge of the transition states.

The atomic configuration corresponding to a chemisorbed S oxygen state at a 7–5–5–7 defect is given in the inset of figure 4. Notice that the strained carbon bond and the oxygen bond are perpendicular to the nanotube axis. The chemisorbed oxygen molecule has a bond length ∼1.5 Å and the Mulliken population analysis indicated a transfer of ∼0.4e to the oxygen molecule. The effect of this transfer is to make the nanotube p-like, in accord with experiments (cf figures 1–3). It is important to mention here that Eklund and co-workers [14] have recently measured a charge transfer of 0.2e from the Raman shift of the oxygen stretching mode frequency in doped bundles.

To investigate the dependence of oxygen molecular binding on the chirality of the nanotube, we have also studied the interaction of O_2 with a metallic (5, 5) nanotube whose

diameter differs by ∼15% relative to that of a $(10, 0)$ tube. Our results suggest a similar binding energy and activation barrier energetics as those obtained for a $(10, 0)$ nanotube, implying that chirality plays an insignificant role as far as interaction of O_2 with a nanotube is concerned.

The chemisorbed state is reversible, since the barrier (1.2 eV from figure 4) can also be crossed in the reverse direction, explaining why oxygen is desorbed when nanotubes are heated to ∼400 K in vacuum ($∼10^{-5}$ Torr). A very interesting result of the calculation is that the barrier to chemisorption is substantially reduced if the oxygen molecule can be prepared in the S state. Singlet oxygen could be generated through interaction of carbon nanotubes with triplet oxygen when nanotubes were excited with UV light. Similar photoinduced doping of oxygen was previously reported in solid C_{60} films [15, 16]. In the case of C_{60}, the incident photons promote the C_{60} molecules from the singlet ground state to the lowest excited triplet state which has a lifetime of ∼40 μs [17]. In the presence of molecular oxygen (whose ground state is a triplet), the lowest excited triplet state of C_{60} is quenched through energy exchange with oxygen, forming S oxygen. In the presence of defects on the tube walls, it may be possible to pump nanotubes into the lowest excited triplet state. For carbon nanotubes, the quenching of photoexcited states by electron donors has been reported [18] and so has the formation of emissive charge-transfer species of carbon nanotubes with electron-rich anilines [19]. These results collectively are supportive of the notion that carbon nanotubes, in the presence of defects, exhibit interesting photochemical properties that warrant further studies.

The photoinduced oxygen adsorption may also be explained in terms of changes in the surface electronic structure upon UV illumination, which are associated with the characteristic charge transfer properties of nanoscale carbon materials. The likely presence of defects in carbon nanotubes may facilitate the formation of locally electron-deficient and electron-rich regions on the nanotubes, similar to the high polarizability that has been reported for polymerized fullerenes [20]. Upon UV illumination there could be intra-nanotube electron shifts (polarization or charge redistribution), which exaggerate the locally charged surface characteristics and thus facilitate the adsorption of oxygen molecules on the nanotubes. Oxygen chemisorption stabilizes the nanotube surface and effectively traps the local charges resulting from UV illumination. Thus, it may be expected that desorption of oxygen molecules from the nanotube surface should also be promoted under illumination and vacuum conditions. Recently, a photoinduced *desorption* of oxygen in air-exposed SWNTs has been reported by Dai and co-workers [21]. The electrical conductance of their SWNT sample performed under vacuum (10^{-8} Torr) decreased dramatically by three orders of magnitude upon UV illumination ($\lambda = 248$ nm). They suggest that the photodesorption effect is due to a non-thermal process that is mediated by electronic transitions in carbon nanotubes, such as photoexcited π-electron plasmons in nanotubes ∼5 eV.

We conclude with a few remarks. In the present study our theoretical analysis performed on both graphene and nanotube structures with limited defect types suggest that the activated nature of the chemisorbed state plays an essential role in explaining the experimental observations of photoinduced oxidation. Experiments involving magnetic fields, like electron spin resonance (ESR) measurements, could further confirm the proposed mechanisms. For example, ESR experiments performed on carbon nanotubes oxidized in the presence of UV light, should show relatively higher concentrations of singlet oxygen compared to nanotubes oxidized under room light.

Acknowledgments

References

[1] Collins P G, Bradley K, Ishigsmi M and Zettl A 2000 Extreme oxygen sensitivity of electronic properties of carbon nanotubes *Science* **287** 1801

[2] Sumanasekera G U, Adu C K W, Fang S and Eklund P C 2000 Effects of gas adsorption and collisions on electrical transport in single-walled carbon nanotubes *Phys. Rev. Lett.* **85** 1096

[3] Bradley K, Jhi S-H, Collins P G, Hone J, Cohen M L, Louie S G and Zettl A 2000 Is the intrinsic thermoelectric power of carbon nanotubes positive? *Phys. Rev. Lett.* **85** 4361

[4] Avouris Ph, Martel R, Derycke V and Appenzeller J 2002 Carbon nanotube transistors and logic gates *Physica B* **323** 6

[5] Andrews R, Jacques D, Rao A M, Derbyshire F, Qian D, Fan X, Dickey E C and Chen J 1999 Continuous production of aligned carbon nanotubes: a step closer to commercial realization *Chem. Phys. Lett.* **303** 467

[6] Hohenberg P and Kohn W 1964 Inhomogeneous electron gas *Phys. Rev.* B **136** B864

[7] Laasonen K, Pasquarello A, Car R, Lee C and Vanderbilt D 1993 Car–Parrinello molecular dynamics with Vanderbilt ultrasoft pseudopotentials *Phys. Rev.* B **47** 10142

[8] Jhi S H, Louie S G and Cohen M L 2000 Electronic properties of oxidized carbon nanotubes *Phys. Rev. Lett.* **85** 1710

[9] Giannozzi P, Car R and Scoles G 2003 Oxygen adsorption on graphite and nanotubes *J. Chem. Phys.* **118** 1003

[10] Sorescu D C, Jordan K D and Avouris P 2001 Theoretical study of oxygen adsorption on graphite and the (8, 0) single-walled carbon nanotube *J. Phys. B: At. Mol. Opt. Phys.* **105** 11227

[11] Stone A J and Wales D J 1986 Theoretical studies of icosadehral C_{60} and some related species *Chem. Phys. Lett.* **128** 501

[12] Perdew J P, Burke S and Ernzerhof M 1996 Generalized gradient approximation made simple *Phys. Rev. Lett.* **77** 3865

[13] Kohn W and Sham L J 1965 Self-consistent equations including exchange and correlation effects *Phys. Rev.* **140** A1133

[14] Eklund P C, private communication

[15] Rao A M, Wang K A, Holden J M, Wang Y, Zhou P, Eklund P C, Eloi C C and Robertson J D 1993 Photoassisted oxygen doping of C_{60} films *J. Mater. Res.* **8** 2277

[16] Eloi C C, Robertson J D, Rao A M, Zhou P, Wang K A and Eklund P C 1993 An investigation of photoassisted diffusion of oxygen in solid C_{60} films using resonant alpha-scattering *J. Mater. Res.* **8** 3085

[17] Haufler R E, Wang L S, Chibante L P F, Jin C M, Conceicao J J, Chai Y and Smalley R E 1991 Fullerene triplet state production and decay: R2PI probes of C_{60} and C_{70} in a supersonic beam *Chem. Phys. Lett.* **179** 449

[18] Riggs J E, Guo Z, Carroll D L and Sun Y-P 2000 Strong luminescence of solubilized carbon nanotubes *J. Am. Chem. Soc.* **122** 5879

[19] Sun Y, Wilson S R and Schuster D I 2001 High dissolution and strong light emission of carbon nanotubes in aromatic amine solvents *J. Am. Chem. Soc.* **123** 5348

[20] Ma B 1998 *PhD Dissertation* Clemson University

[21] Chen R J, Franklin N R, Kong J, Cao J, Tombler T W, Zhang Y and Dai H 2001 Molecular photodesorption from single-walled carbon nanotubes *Appl. Phys. Lett.* **79** 2258